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(19)



(54) PROCESS FOR ISOMERIZING ALKYLATED BENZENES

(71) We, ENGELHARD MINERALS & CHEMICALS CORPORATION, of 430 Mountain Avenue, Murray Hill, New Jersey, United States of America, formerly of 113 Astor Street, Newark, New Jersey, United States of America, a corporation organized under the laws of the State of Delaware, one of the United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for isomerizing an alkylated benzene containing from 8 to 10 carbon atoms and having two or more alkyl substituents each of which is a methyl or ethyl group, or a mixture of such benzenes.

There is substantial interest in the isomerization of such benzenes, which are exemplified by the xylenes, particularly hydrocarbon mixtures rich in meta-xylene and having less than an equilibrium amount of para-xylene and often a minor amount of ethylbenzene. During the isomerization, the meta-xylene-rich mixtures are converted to reaction products containing greater amounts of para-xylene, the latter isomer being separated from the reaction product by crystallization or extraction and employed, after oxidation, in the manufacture of polymers. The product may also be reduced in ethylbenzene content compared with the starting mixture. Other suitable alkylated benzenes include pseudocumene and prehnitene. The various alkylated benzenes are usually available in forms containing less than about 10 ppm by weight sulphur, often less than about 1 ppm. One example of this type of isomerization is described in U.S. Patent No. 2,976,332, wherein a catalyst containing a platinum on alumina component which is physically mixed with a silica-alumina cracking component is used. In the isomerization, the alkylated benzene feeds, which contain a non-equilibrium amount of

isomers of the alkylated benzene taken on the basis of the ratio that would be present in thermodynamic equilibrium at the isomerization temperature, are converted to a mixture of isomers more closely approximating the equilibrium amounts. If desired, a selected isomer or mixture of isomers can be separated from the product and remaining materials recycled to the reaction zone for isomerization along with fresh alkylated benzene feed.

According to the present invention, there is provided a process for isomerizing an alkylated benzene containing from 8 to 10 carbon atoms and having two or more alkyl substituents each of which is a methyl or ethyl group, or a mixture of such benzenes, which comprises isomerizing the benzene or mixture in the presence of molecular hydrogen and in contact with a catalyst comprising minor amounts of a platinum series metal (as hereinafter defined) and rhenium supported upon a major amount of a porous, solid oxidic support having an average tertiary butylbenzene dealkylation activity at 455°C (without water addition) of at least 20 cubic centimeters (STP) per gram per minute, as measured by the method referred to hereinafter.

As used herein, the term "platinum series metal" means metals of the platinum triad (i.e. osmium, iridium and platinum) and metals of the palladium triad (i.e. ruthenium, rhodium and palladium).

The support of the catalyst employed in the process of this invention is a solid, porous oxidic support which exhibits a substantial average acidity, i.e., a tertiary butylbenzene dealkylation activity of at least 20 cubic centimeters (STP) per gram per minute at 455°C (without water addition). The tertiary butylbenzene dealkylation activities given herein are measured by the method of Marvin F. L. Johnson and John S. Malik, as published in "Dealkylation of t-Butylbenzene by Cracking Catalysts", Journal of Physical Chemistry, Vol. 65, pp. 1146—1150

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(1961). Preferably, such activity is from 400 to 1200.

It is preferred that the catalyst be a physical admixture of (a) particles of a porous, solid oxidic support of relatively low, if any, acidity (e.g. an alumina support) on which the platinum series metal and rhenium are supported, and (b) particles of a porous, solid oxidic support exhibiting substantial acidity but low in hydrogenation-dehydrogenation activity (e.g. a silica-alumina support, a crystalline aluminosilicate support of relatively large pore size, or mixtures thereof). However, other forms of catalyst can be employed. Thus, for example, either the platinum series metal or rhenium used as promoters can be supported on the relatively non-acidic support while the other of the platinum series metal or rhenium is supported by the support of higher acidity. Also, the relatively non-acidic support and the support of higher acidity can be mixed to form a composite support on which the platinum series metal and rhenium are then deposited. In another alternative form of the catalyst, both the platinum series metal and rhenium can be disposed on the support of higher acidity and then the composite physically mixed with a solid, porous oxidic support of low acidity to give an overall catalyst having the desired average acidity. In the latter type of catalyst, the support of higher acidity may be a mixture of silica-aluminas with the platinum series metal and rhenium being on either or both of the silica-alumina particle types. For instance, it can be advantageous if the platinum series metal is supported on a silica-alumina support containing from 10 to 20 weight % alumina while the rhenium is supported on a silica-alumina support having an alumina content of from 25 to 40 weight %.

The catalyst employed in the process of this invention has on an overall or average basis, minor amounts of the platinum series metal and rhenium. The amount of each present is preferably from 0.1 to 2.5 weight % of the overall catalyst, more preferably from 0.2 to 1 weight %. Although various platinum series metals can be used in the catalyst, for instance platinum, palladium, or rhodium, platinum is preferred.

The major portion of the catalyst employed in the isomerization process of this invention is the solid, porous oxidic support. The total amount of support can be, for example, from 95 to 99.8 weight % of the catalyst, although it can be a lesser portion of the catalyst, but usually at least 90 weight %, as the result of the presence of materials other than the platinum series metal and rhenium. The platinum series metal and rhenium can, and preferably are, in elemental state when the catalyst is used

in the reaction; however, they may also be in combined form such as their oxides or sulphides. It is preferred that the platinum series metal and rhenium in the catalysts are not detectable by X-ray diffraction analysis which means that if the metals be present in the elemental state, their crystallite sizes are less than about 50 Å as determined by X-ray techniques.

One method of providing the platinum series metal in the catalyst is by contact of the support, either in hydrous or in calcined form, with an aqueous solution of a halogen-containing compound, for instance chloroplatinic acid. In this manner, halogen is incorporated in the catalyst, for instance, in amounts of from 0.2 to 2 weight %, preferably from 0.3 to 1 weight %. Such amounts of halogen, e.g. chlorine, can also be provided in the catalyst from a source other than the compound supplying the platinum series metal. Rhenium can also be added to the hydrous or calcined support through contact with an aqueous solution of rhenium compound, e.g. perrhenic acid or ammonium perrhenate. If the platinum series metal or rhenium is added to a calcined support, the resulting composite is generally recalcined. Calcination of the catalysts used in this invention can be conveniently conducted at temperatures of from 700 to 1200°F, for instance in an oxygen-containing gas, and this operation can be controlled to give a final analysis of desired surface area.

The support of the catalyst is of selected characteristics in order to provide the desired acidity and generally with low hydrogenation-dehydrogenation activity. The support usually consists of a mixture of metal oxides, the metals of which are preferably selected from Groups II to IV of the Periodic Table. Examples of such metal oxides are silica, alumina, titania, zirconia, magnesia, and their mixtures. The support can consist of clays, and synthetic and natural amorphous or crystalline aluminosilicates, and their mixtures. It is especially preferred that the support contain both silica and alumina in some form, especially the support of relatively high acidity. Also, the catalyst may have minor amounts of non-metal components, especially those which enhance acidic activity such as boria and the halogens, for instance, fluorine and chlorine.

Most advantageously, the support comprises a mixture of materials of more or less distinct types, that is, a mixture of a relatively low acidity oxidic support exhibiting a tertiary butylbenzene dealkylation acidity of up to 15, preferably up to 10, with a relatively high acidity oxidic support having a tertiary butylbenzene dealkylation activity of at least 30, preferably

- at least 500. The amounts of these separate supports present are such as to give an overall porous oxidic support of the required average acidity. The amounts are usually from 10 to 90 weight % of each. The relatively high acidity support can be from 0.5 to 95 weight % of the catalyst, preferably from 10 to 70 weight %. For example, the total support may contain from 30 to 95 weight % of amorphous silica-alumina, preferably from 40 to 70 weight %, with the essential balance of the support being composed of the relatively non-acidic or low activity component, for instance, alumina. As another example, the support can be composed of from 1 to 50 weight %, preferably from 10 to 30 weight %, of an acidic material containing a mixture of crystalline aluminosilicate and amorphous silica-alumina in which the crystalline aluminosilicate is from 5 to 25 weight %, the remaining portion of the support being essentially a lower activity material such as alumina. As a further alternative the support can contain from 0.5 to 40 weight %, preferably from 10 to 25 weight %, of a crystalline aluminosilicate, with the essential balance of the support being alumina.
- The various porous oxidic supports which can be used are available in many forms. These supports are generally of relatively high surface area and usually have a BET surface area as determined by the nitrogen absorption method [JACS, Volume 60, beginning at page 309 (1938)] of at least 100 square meters per gram. As a relatively low acidity support, alumina is particularly preferred and it can be in one or a mixture of the activated forms known as gamma family aluminas such as chi, gamma and eta aluminas.
- The alumina supports which can be present in the catalyst used in the process of the invention preferably have a surface area of at least 150 square meters per gram and is preferably composed to a major extent of gamma-family alumina modifications derived by the activation or calcination of alumina trihydrates. These gamma-family or activated alumina modifications include among others, gamma and eta aluminas. U.S. Patent No. 2,838,444 discloses this type of alumina support having surface areas in the range of from 350 to 550 square meters per gram, while in U.S. Patent No. 2,838,445 there is described catalyst supports made from predominantly trihydrate alumina precursors, the supports having surface areas in the range of from 150 to 350 square meters per gram. These supports are suitable for use in the present invention, especially the higher area supports of U.S. Patent No. 2,838,444 which supports during use may have their surface areas reduced to, for instance, from 150 to 250 square meters per gram. As stated, the preferred alumina precursors predominate in trihydrate which may contain one or more of the bayerite, gibbsite or nordstrandite (previously called randomite) forms, and preferably a major amount of the trihydrate is composed of bayerite or nordstrandite which when calcined can form eta alumina. It is also advantageous that the hydrous alumina precursor contain from 65 to 95% of the trihydrate with the essential balance being composed by one or both of the alumina monohydrate, boehmite, or amorphous hydrous alumina. Preferred alumina supports have pore volumes of at least 0.1 cc./gm., preferably at least 0.15 cc./gm., in pores greater than 100 Å radius. It is also preferred that these supports have at least 0.05 cc./gm. in pores greater than 300 Å or even greater than 600 Å radius. These determinations are by the method described by Barrett, Joyner and Halenda, JACS, 73, p. 373 (1951).
- The amorphous silica-alumina supports which can be present in the catalyst employed in the process of this invention are available in several forms. These supports usually contain from 10 to 40 weight % alumina with the essential balance being silica, although minor amounts of other components such as metal oxides may be present. These silica-alumina supports after calcination usually have surface areas of from 100 to 500 square meters per gram.
- Other types of silica-alumina supports which can be present in the catalyst are the natural and synthetic crystalline aluminosilicate supports. These supports are of the relatively large pore variety, that is, having relatively uniform pore openings with a minimum diameter of 10 Å, for instance, 10 to 15 Å, preferably 12 to 14 Å. The mole ratio of silica-to-alumina in these supports is usually at least 2:1 up to 12:1. However, the preferred crystalline aluminosilicate supports have silica-to-alumina mole ratios of from 2 to 6:1, or from 4 to 6:1, such as those of the faujasite type. The various crystalline aluminosilicate supports are usually available or made in the sodium form and generally it is desired to reduce the sodium content of these supports so that it is less than 4 weight %, preferably less than 1 weight %, of the crystalline aluminosilicate. The amount of sodium can be reduced through exchange with hydrogen ions, or precursors thereof such as ammonium ions, or with polyvalent metal ions, for instance, those of the rare earth series such as cerium or praseodymium, or their mixtures. Usually, the extent of ion exchange is such that at least 50 mole %, preferably at least 90 mole %, of the sodium is removed.

The isomerization process of this invention can be carried out at temperatures of from 650 to 950°F., preferably from 700 to 900°F. Other suitable reaction conditions include pressures of from 50 to 500 psig, space velocities of from 0.2 to 20, WHSV (weights of hydrocarbon per weight of catalyst per hour) and at molecular hydrogen to hydrocarbon mol ratios of from 3 to 30:1. Preferably, these reaction conditions are from 100 to 350 psig, from 0.5 to 15 WHSV and from 4 to 15:1 hydrogen to hydrocarbon mole ratio. Preferably, the fluid materials in the isomerization reaction zone have less than 100 ppm sulphur, more preferably less than 20 ppm or less than 10 ppm.

In the process of the invention, the catalysts can be employed in any convenient particle size. Thus, the catalyst may be finely divided and employed as fluidized bed, but more preferably the catalyst is macrosized as obtained, for instance, by tableting or extrusion. The macrosized particles usually have diameters of from $\frac{1}{16}$ to $\frac{1}{4}$ inch, preferably from $\frac{1}{32}$ to $\frac{1}{8}$ inch and, if not spherical, lengths of from $\frac{1}{16}$ to one inch or more, preferably from $\frac{1}{8}$ to $\frac{3}{4}$ inch. The macrosized catalyst can be employed as a fixed or moving bed but is normally used as a fixed bed.

Carbonaceous deposits can accumulate on the catalysts as isomerization proceeds, and the catalysts can be regenerated by carbon burn-off which improves the catalytic characteristics sufficiently for the catalysts to be reused on an economic basis. At the beginning of regeneration, the carbon content of the catalysts is generally above 0.5 weight %, usually greater than 3 weight %. During regeneration of the catalysts by burning, the carbon level is usually reduced to below 0.5 weight %, preferably below 0.2 weight %. This burning can be conducted through contact of the catalysts with an oxygen-containing gas and generally the amount of oxygen is controlled to maintain the temperature of the catalysts from 700 to 900 or 1000°F., preferably in the temperature range of from 700 to 850°F. The pressure maintained during burning is preferably elevated, for instance, from 50 to 500 psig. The controlled burning is usually initiated with an inert gas, e.g. nitrogen, carbon dioxide or their mixtures, containing a small amount of oxygen, for instance, up to 1 mole % and preferably with an oxygen partial pressure of at least 0.2 psig. When the bulk of the carbon has been removed from the catalysts by a gas containing the relatively low concentration of oxygen, the amount of oxygen can be increased somewhat to insure that sufficient carbon has been removed from the catalysts without exceeding the desired temperature.

This type of treatment is exemplified by one or more burns-through of a fixed catalyst bed at 800°F. to 850°F., and 100 to 500 psig, with a gas containing above 1 to 3 or somewhat greater mole percent oxygen. Other suitable carbon-burning procedures can be employed as long as the temperatures are controlled and the carbon level of the catalysts is adequately lowered. During carbon burn-off and any subsequent treatments of the catalysts with an oxygen-containing or other gas at elevated temperatures, the gas should be dry enough to avoid undue sintering of the catalysts and loss of surface area. Such loss generally increases as temperature, water content of the gas or treating time is raised.

Especially where the crystallite size of the promoting metals on the catalysts is to be reduced, the catalysts can, after carbon burn-off, be contacted with an oxygen-containing gas at a temperature of from 800 to 1000°F., preferably from 850 to 950°F., and, if desired, an elevated pressure such as from 100 to 500 psig. This treatment can be referred to as an air soak and the oxygen content of the gas is usually greater than that present in the gas employed for carbon burn-off. Thus, the oxygen content of the gaseous stream employed for air soaking is usually at least 5 mole %. However, there has been found no particular reason for increasing the gas content above 20 mole %. The air soaking period is generally at least one hour and is usually continued for several hours, for instance, in the range of from 5 to 24 hours. Regeneration and air soaking procedures suitable for the catalysts are disclosed in U.S. Patent No. 2,922,756.

The virgin catalysts used in this invention or used catalysts of such types, say after regeneration with or without reactivation, can be reduced by contact with a gaseous stream which contains molecular hydrogen. The treatment can be at an elevated temperature, for instance, from 600 to 1000°F., preferably from 750 to 950°F. Elevated pressures are preferably used in the reduction and can be, for example, from 20 to 600 psig, preferably from 50 to 350 psig. Apparently, the reduction converts the catalytic promoting metals to their elemental state, but if a vaporous sulphiding agent be present some or all of the promoting metals may be sulphided. The gas stream employed during reduction is usually composed of from 70 to 100 volume % hydrogen, preferably from 95 or 99 to 100 volume %, with any remaining components being up to 30 volume % of inert gas such as nitrogen. The gas advantageously contains less than 1 volume % hydrocarbons boiling above methane, preferably less than 0.1%.

- To avoid undue hydrocracking of the hydrocarbon feedstock during the initial period of hydrocarbon processing after the catalysts are placed on-stream, the catalysts can be contacted with a gas containing sulphur-providing component in vaporous form. This sulphiding treatment can be conducted simultaneously with or subsequent to the reduction. If sulphiding is conducted simultaneously with the reduction, a non-carbonaceous sulphur compound is preferably used due to the presence of oxygen in the system and to avoid any localized overheating of the catalyst. A suitable sulphur-providing material or sulphiding agent is H_2S . The amount of sulphiding agent employed is at least 25%, preferably at least 50%, of the stoichiometric amount needed to give one atomic weight of sulphur for each atomic weight of total platinum series metal and rhenium in the catalyst. Preferably the amount is at least 50% up to 500% or more. The sulphiding operation can be done at an elevated temperature, e.g. from 650 to 950°F., and at any suitable pressure, preferably an elevated pressure such as from 100 to 500 psig. The sulphiding gas is reductive and usually contains a minor amount of the sulphur-bearing component, e.g. from 0.1—10 volume %, preferably from 0.2 to 3%, with the major component being hydrogen or an inert gas such as nitrogen. When the sulphiding is conducted simultaneously with or subsequent to reducing the catalysts with hydrogen, the catalysts are in sulphided form when they first contact the hydrocarbon being processed which avoids excessive hydrocracking with its attendant yield and selectivity losses.
- It can be further advantageous in minimizing hydrocracking caused by the reduced catalysts whether presulphided or not, to supply vaporous sulphiding agent to the conversion system when charging of the hydrocarbon feedstock is begun. Thus, a small amount of the sulphiding agent, sufficient to significantly reduce hydrocracking during the initial portion of the processing cycle, can be added to the system. The sulphiding agent can conveniently be charged with the recycle gas or with the hydrocarbon stream. The amounts of sulphiding agent employed are usually from 1 to 500 ppm by volume based on the hydrogen passing to the reaction system, preferably from 5 to 200 ppm. This sulphiding-agent addition can be continued as long as the operator desires but often the addition will approximate the time period in which, in the absence of the sulphiding-agent addition, the catalysts would cause significantly excessive hydrocracking. The period of sulphiding-agent addition upon placing the reduced catalysts back on processing can be, for instance, from 1 to 60 or more days and is usually from 3 to 10 days.
- It may also be advantageous to incorporate in the reaction system a small amount of ammonia or a material which is decomposed under the reaction conditions to supply ammonia such as the lower alkyl amines, for instance, butyl amine. The ammonia can serve to give better catalyst performance during an initial period of relatively high activity in order that the desired selectivity can be obtained, for instance, an approach of at least 95% towards equilibrium. The amount of ammonia is usually from 5 to 200 parts per million by weight based on the alkylated benzene feed, preferably from 10 to 100 parts per million. As the reaction proceeds it may be necessary to decrease the amount of ammonia and to even omit its introduction entirely in order to obtain an adequate approach to equilibrium. It may be advantageous to enhance the activity of the system by providing from 5 to 200 ppm water based on the weight of the alkylated benzene feed, preferably from 25 to 75 ppm. The water may be especially desired when the overall supports of the catalyst have a tertiary butylbenzene dealkylation activity of below 30. The invention will now be illustrated by the following Example.
- ### EXAMPLE
- The following catalysts were evaluated in the isomerization of xylenes:
- Catalyst A* — This catalyst was a physical admixture of spray-dried alumina having impregnated therein 0.6% platinum and 0.6% rhenium (calcined basis), the alumina, whose t-butylbenzene dealkylation activity was 13, being a mixture of
- | | |
|-------------------------------|-----|
| 45% bayerite, | |
| 10% gibbsite, | |
| 20% nordstrandite, | 110 |
| 22% boehmite and | |
| 3% amorphous hydrous alumina; | |
- with about an equal amount by weight (on an ignited weight basis) of spray-dried, microspherical, amorphous silica-alumina cracking catalyst containing about 12 weight % alumina and after partial deactivation and calcination having a t-butylbenzene dealkylation activity of about 1600. The mixture, containing sufficient water to provide an extrudable consistency, was extruded into particles $\frac{1}{16}$ inch in diameter and about $\frac{1}{4}$ to $\frac{3}{4}$ inch in length. The extruded particles were dried and then calcined in a stream of dry air at 900°F. for three hours. The calcined particles had a surface area of about 400 square meters per gram, and a calcined composite of the alumina and silica-alumina in the catalyst, that is, on a non-platinum,

non-rhenium basis, exhibited a *t*-butylbenzene dealkylation activity of about 800.

Catalyst B — This catalyst was made by impregnating a spray-dried alumina containing about 75% boehmite having a crystallite size of 35 Å., and about 25% amorphous hydrous alumina with 0.7% platinum and 0.5% rhenium (calcined basis). The impregnated alumina (*t*-butylbenzene dealkylation activity of 5) was mixed with 25% based on the total ignited weight of an ammonium-exchanged, crystalline aluminosilicate of the faujasite type having a silica-to-alumina mole ratio of 4.5:1 and pore openings of 13 Å diameter. The mixture was combined with water to give a material of extrusion consistency and was extruded into particles of the same size as those of Catalyst A. These particles were calcined in the manner of Catalyst A and the calcined catalyst had a surface area of about 375 square meters per gram. A calcined composite of the alumina and aluminosilicate of the catalyst, that is on a non-platinum, non-rhenium basis, had a *t*-butylbenzene dealkylation activity of about 1000 after calcination.

Each of catalysts A and B was evaluated in the isomerization of xylenes. The catalyst was disposed in the reactor as a fixed bed and was prereduced in hydrogen at about 900°F. The xylene feedstock contained about 7 weight % para-xylene, 46 weight % meta-xylene, 38 weight % ortho-xylene, 5% ethylbenzene, 4% total paraffins and cyclo-paraffins and essentially no sulphur. The isomerizations were conducted at about 820°F., 175 psig, 2 WHSV and 5:1 hydrogen to hydrocarbon mole ratio. Both catalysts A and B when used in the isomerization system gave an approach to equilibrium in the range of 95 to 98% and the product contained less than 4 weight % increase in hydrocarbons boiling below the C₈ range. The catalyst also exhibited good life and relatively low coke formation during the isomerization.

WHAT WE CLAIM IS:—

1. A process for isomerizing an alkylated benzene containing from 8 to 10 carbon atoms and having two or more alkyl substituents each of which is a methyl or ethyl group, or a mixture of such benzenes, which comprises isomerizing the benzene or mixture in the presence of molecular hydrogen and in contact with a catalyst comprising minor amounts of a platinum series metal (as hereinbefore defined) and rhenium supported upon a major amount of a porous, solid oxidic support having an average tertiary butylbenzene dealkylation activity at 455°C (without water addition) of at least 20 cubic centimeters (STP) per gram per minute, as measured by the method referred to hereinbefore.

2. A process according to claim 1, in which the benzene or mixture is isomerized at a temperature of from 650 to 950°F.

3. A process according to claim 2, in which the benzene or mixture is isomerized at a temperature of from 700 to 900°F.

4. A process according to any one of the preceding claims, in which the benzene or mixture is isomerized at a pressure of from 50 to 500 psig.

5. A process according to claim 4, in which the benzene or mixture is isomerized at a pressure of from 100 to 350 psig.

6. A process according to any one of the preceding claims, in which the catalyst contains from 0.2 to 1% by weight of the platinum series metal.

7. A process according to any one of the preceding claims, in which the catalyst contains from 0.2 to 1% by weight of rhenium.

8. A process according to any one of the preceding claims, in which the platinum series metal is platinum.

9. A process according to any one of the preceding claims, in which the support has a surface area of at least 100 square meters per gram.

10. A process according to any one of the preceding claims, in which the catalyst comprises an admixture of (a) particles of a porous, solid, oxidic support having a tertiary butylbenzene dealkylation activity at 455°C (without water addition) of up to 15 cubic centimetres (STP) per gram per minute, measured by the method referred to hereinbefore, which particles have the platinum series metal and the rhenium supported thereon, and (b) particles of a solid, oxidic support having a tertiary butylbenzene dealkylation activity at 455°C (without water addition) of at least 30 cubic centimeters (STP) per gram per minute, as measured by the method referred to hereinbefore.

11. A process according to claim 10, in which the support having the lower activity is an alumina support.

12. A process according to claim 11, in which the alumina support is obtained by calcination of hydrous alumina which is predominantly the trihydrate form.

13. A process according to any one of claims 10 to 12, in which the support having the higher activity is an amorphous silica-alumina support or a crystalline aluminosilicate support.

14. A process according to claim 13, in which the crystalline aluminosilicate support has a silica-to-alumina mole ratio of from 2:1 to 6:1, pores of from 10 to 15 Å in diameter, and a sodium content of less than 1% by weight.

15. A process according to any one of the preceding claims, in which the mixture is a mixture of xylenes containing meta-xylene

and less than an equilibrium amount of para-xylene.

- 5 16. A process in accordance with claim 1 for isomerizing an alkylated benzene hydrocarbon, substantially as described in the foregoing Example.

17. The product of a process claimed in any one of the preceding claims.

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